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MIRRORING NUTRIENT CYCLES IN A FORESTED WATERSHED BY STREAM  
WATER COMPOSITION

Henri Laudelout<sup>1</sup>, Pierre André<sup>2</sup> and Catherine Legrand-Marco<sup>1</sup>

<sup>1</sup>Université Catholique de Louvain, Faculté des Sciences  
Agronomiques, Département des Sciences du Sol, Place Croix du  
Sud, 2, B-1348 Louvain-la-Neuve, Belgique.

<sup>2</sup>Université Catholique de Louvain, Faculté des Sciences  
Agronomiques, Département des Eaux et Forêts, Place Croix du  
Sud, 2, B-1348 Louvain-la-Neuve, Belgique.

ABSTRACT

This paper presents data on stream water composition in a forested watershed (Querceto-carpinetum) as influenced by seasons and properties of the A horizons. Increased residence time of water in these horizons causes an increase in Ca and Mg bicarbonates concentration in direct relation to their proportion on the exchange sites in the soil. The mechanism is attributed to an exchange between H<sup>+</sup> ions and soil cations and spontaneous evolution of H<sup>+</sup> clays to Al-clays. Calculation of P<sub>CO<sub>2</sub></sub> in the soil from stream water composition seems to show that flushing the soil atmosphere by rainfall and return of organic matter to the soil during litterfall are predominating factors. Nitrate is as usual low during the growing season and becomes higher in Wintertime.

INTRODUCTION

The ecosystem-watershed concept is relatively new and has proved itself to be one of the most fruitful approach of the last two decades. There are several facets to its use, one of them being the biogeochemistry of stream water which mirrors the processes occurring in the various soil horizons and in the weathering zone, given an initial composition of the input water. If the lower horizons are fairly impermeable and the bedrock totally impervious, then the stream water composition should be a faithful reflection of the processes occurring in the A horizons which are determined to a large extent by the nutrient cycles between soil and vegetation.

This is due to the fact that with impervious B horizons and bedrock, most of the flow will occur as subsurface runoff towards

the stream. The residence time of water in the unsaturated zone will vary according to the frequency and abundance of rainfall and its composition will change at a rate which will be mostly influenced by temperature. The buffering effect of these factors is so important that stream water composition varies relatively little in response to flow rate changes which may comprise several order of magnitudes.

It is the purpose of this communication to present data on the seasonal changes of stream water composition and to attempt to relate them to the properties of the soils found in the watershed studied.

#### EXPERIMENTAL

The watershed studied is drained by the brook "Ruisseau d'Os-tenne" which is an affluent of the Helpe Majeure, the latter joining the Sambre river a few kilometers upstream of Maubeuge (Nord, France).

The watershed is located 180 km N.E. of Paris near the small city of Chimay and covers an area of about 1,000 ha. All of its area is underlaid by Famennian slates from which thin soils heavy in texture have originated.

The bedrock and even the B and C horizons may be considered as practically impervious. On the other hand, the A horizons are well structured and very permeable so that no surface runoff is noticeable even during heavy storms.

Inputs from the atmosphere have been studied by Duvigneaud and al. (1964, 1970, 1971) and Denæyer-De Smet (1966, 1967) on a site located a few km from the watershed in Virelles within the same township of Chimay. Extensive data have been presented by these authors on climatological and vegetation data which need not be repeated here. More general studies on the vegetation of this region may be found in Roisin (1962). Some spot checks on the composition of rain water were made mainly in order to verify whether the  $H^+$  ion content had not increased in later years. Freshly collected rain water had a pH of around 5.8 which points to the unlikelihood of frequent acid rains. Rainfall was measured with 3 rain gauges and 2 pluviographs spread over an area three to four times that of the watershed. The watershed is 95 percent forested, most of the forest vegetation consisting of oak (*Quercus robur*) with an understory of hornbeam (*Carpinus betulus*) coppice which is cut every 20 to 25 years. Pure stands of conifers are represented here and there but are of very little importance. The part of the watershed which is not forested is under permanent pasture.

Samples of stream water were collected at irregular intervals from 1979 to 1983. A first sampling period extended from the Autumn of 1979 to the Spring of 1981 and was followed by two periods of more intensive sampling (twice weekly). The last one which will reported here in some details extending from August 1982 to March 1983.

Ca, Mg, K and Na were determined by atomic absorption spectropho-

tometry using La for minimizing interferences. Nitrate and chloride were determined with specific electrodes by interpolating the potentiometric readings from standard curves and checking for interferences by running recovery tests. Bicarbonate content was set equal to the result of titration of a 100 ml sample with 0.1 M HCl to the methyl orange end point. Conductivity of the stream water was measured at the laboratory temperature and corrected to 20°C. Sulphate was determined by precipitation of  $BaSO_4$  and turbidimetry of the precipitated suspension.

#### RESULTS

Fig. 1 shows that even though outflow could vary by two orders of magnitude after a rainstorm, the total electrolyte content of stream water as measured by its electrical conductivity remained constant within a factor of two. The influence of rain on concentration was, however, noticeable even though it was far from proportional. This is shown by fig. 1, where the amount of rain has been summed over 5-day periods. Clearly, an amount of rain equivalent to 50 mm or more according to the previous moisture status will send the conductivity value down to 150  $\mu$ mhos while a drought period will make it increase to about 250 or 270. This represents an increase of 1.1 mE of salt per l. The nature of the salt responsible for this increase can be deduced from the data

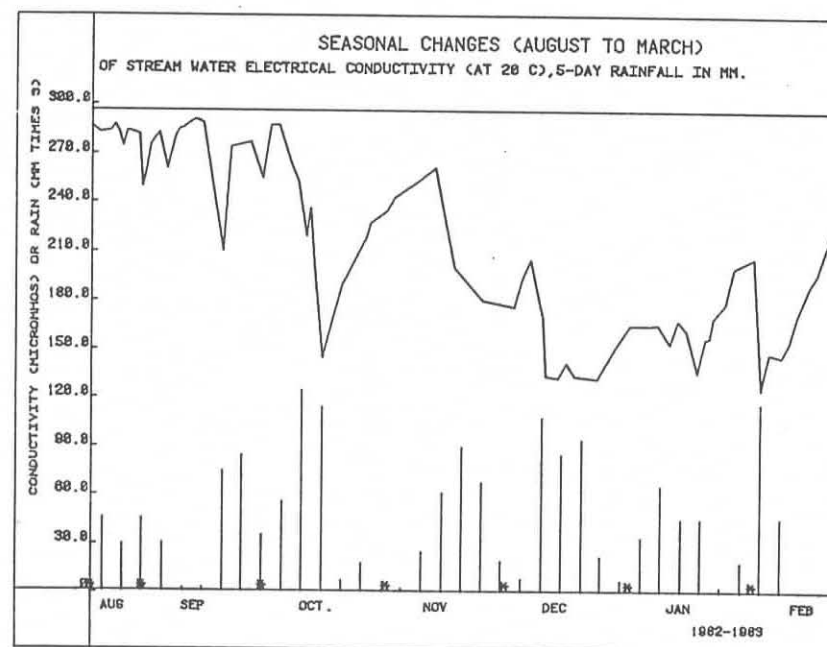


Figure 1.

represented in fig. 2 and 3. The regression of the electrical conductivity at 20°C on the bicarbonate content shows that it is the increase in bicarbonate which determines the increase in salt content. On the other hand, the correlation between bicarbonate and calcium content is also good which means that the increase in conductivity associated with decreased flow rates is caused mainly by an increased concentration in calcium bicarbonate.

The coefficient of the regression of bicarbonate on calcium concentration is 1.58, if  $\text{Ca}^{++}$  was the only cation balancing the increased  $\text{HCO}_3^-$  concentration, it should be unity. Calculating the regression coefficient of bicarbonate concentration on the sum of cations shows that the regression coefficient is close to unity (in fact, we obtain  $\text{HCO}_3^- = 0.683 + 0.98 \times (\text{Ca} + \text{Mg} + \text{K} + \text{Na})$ ).

Since as mentioned earlier, most of the hillslope flow occurs through subsurface runoff, it was deemed interesting to establish the content in exchangeable cations of the upper horizons. Table I presents the values observed for a representative soil profiles.

The fraction of  $\text{Ca}^{++}$  in the total alkali and earth alkali cations in the surface horizons was on average 64%, that of  $\text{Mg}^{++}$  20.6 leaving 15% for  $\text{K}^+$  and  $\text{Na}^+$  of which  $\text{Na}^+$  occupied 1 to 2%. When we compare these proportions with the grand average of stream-water composition, we find 62% of  $\text{Ca}^{++}$  and 20% of  $\text{Mg}^{++}$  among the total cations leaving 18% for  $\text{K}^+$  and  $\text{Na}^+$  of which K occupies 3% only.

Changes in pH of the streamwater were confined to the range of 7.9 to 6.6. They are more interesting when combined with the bicarbonate concentration according to the following equation :

$$\text{pH} + \text{pHCO}_3^- - 7.82 = -\log P_{\text{CO}_2}$$

where  $\text{pHCO}_3^-$  is the negative logarithm of the molar bicarbonate concentration and  $P_{\text{CO}_2}$  is the partial pressure of  $\text{CO}_2$  in atmospheres corresponding at equilibrium to the  $\text{H}^+$  and  $\text{HCO}_3^-$  concentrations.

Table I. Typical analytical data for the upper horizons of a soil profile in the watershed.

Horizon	A <sub>1</sub>	B <sub>g</sub>	BC <sub>g</sub>
Depth	0-4	4-24	24-35
Stoniness (%)	0	0	33
Clay (0-2μ)	42	31	45
C %	4.94	0.94	0.36
N %	0.46	0.11	0.07
C/N	11	8	5
Ca (mE %)	2.49	0.61	1.75
Mg	0.66	0.30	1.94
K	0.53	0.13	0.24
Na	0.07	0.02	0.05
Al	4.95	5.14	2.45
CEC (mE %)	22.6	12.1	14.9
pH	4.6	4.8	4.9

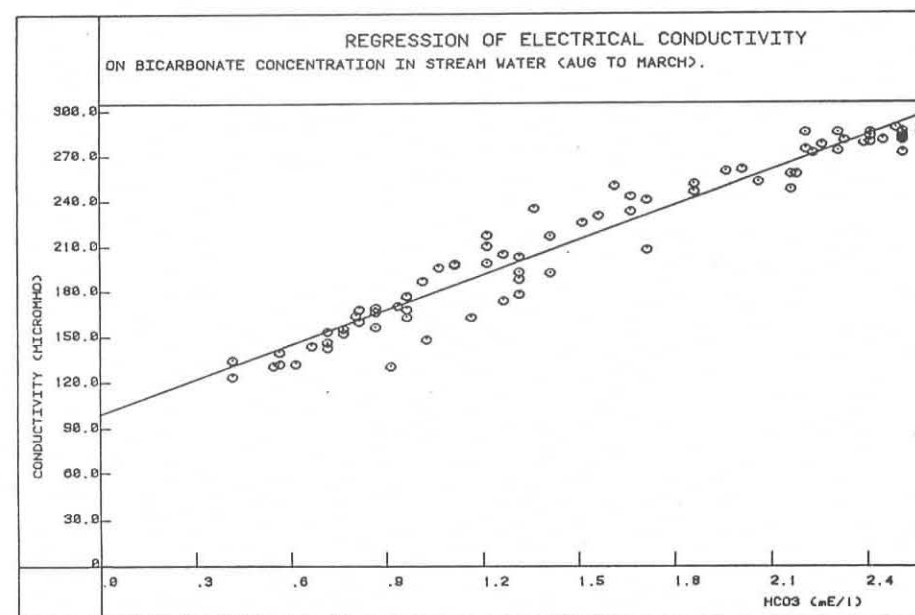


Figure 2.

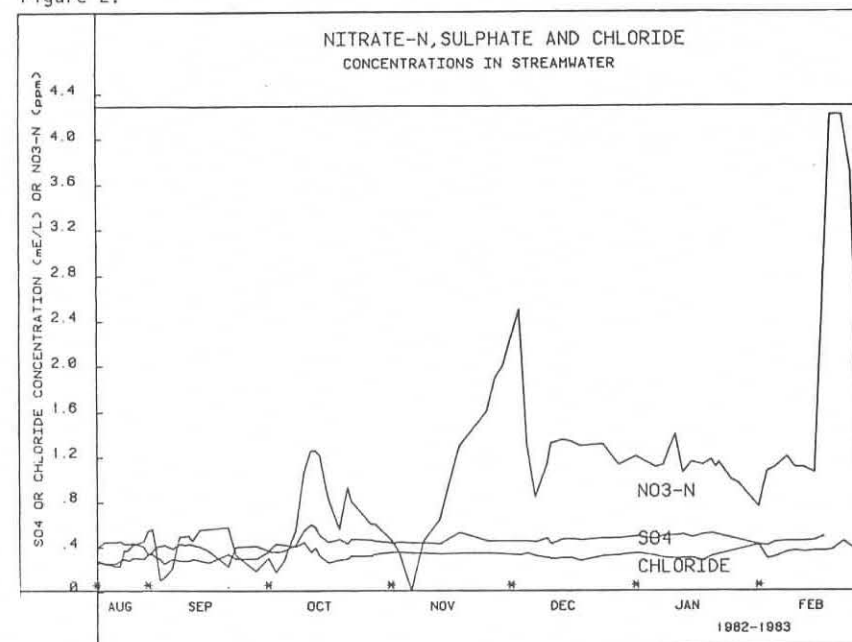


Figure 3.

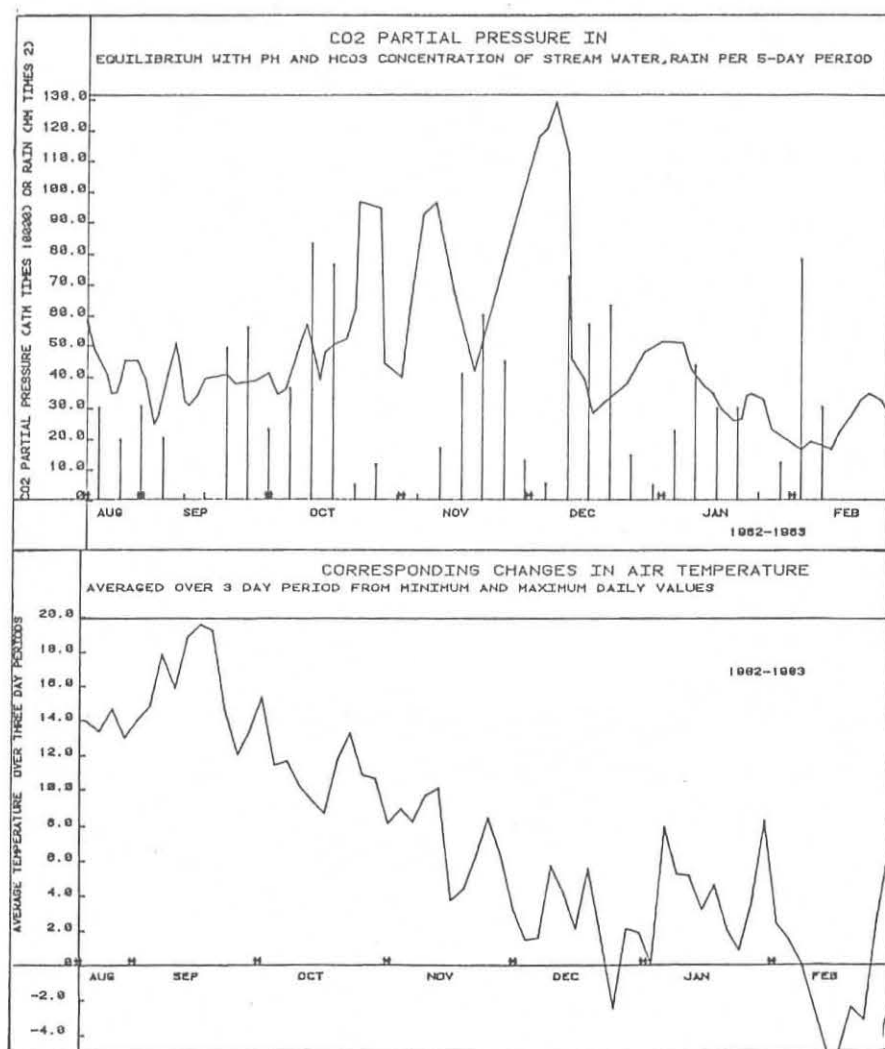


Figure 4.

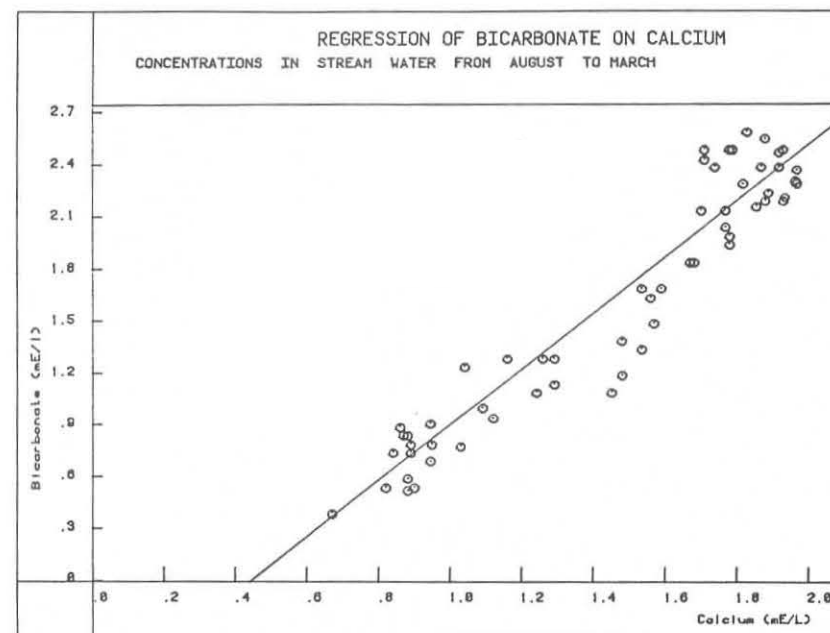


Figure 5.

Activity corrections have been neglected in the above expression which is legitimated by the fact that the ionic strength of the solution is low and that singly charged ions only are considered. Fig. 4 shows the evolution of  $\text{CO}_2$  partial pressure with the 5-day-rainfall and the daily average temperature averaged over three day-periods. The average balance between cations ( $\text{Ca} + \text{Mg} + \text{K} + \text{Na}$ ) and anions ( $\text{HCO}_3 + \text{SO}_4 + \text{Cl} + \text{NO}_3$ ) is 57  $\mu\text{E}$  per l in favour of the anions, which is negligible with respect to the total cationic concentration of 2.28 mE per l. Unmeasured cations could possibly account for the difference since aluminium is a major cation among the exchangeable cations in the forest soil. Considering the average sulphate and hydrogen ion concentrations, a very low concentration of aluminium in water may be calculated using the dissociation constant quoted by Nordstrom (1982).

Bicarbonate is the dominating anion since it accounts for 65% of the total ( $\text{HCO}_3 + \text{SO}_4 + \text{Cl} + \text{NO}_3$ ). Sulphate represents 17% of the sum and chloride 15%. As shown in fig. 5, their seasonal changes are not very important.

Nitrate does fluctuate according to season following the well known pattern of low concentrations during the growing season and higher concentration in Wintertime. Its contribution towards balancing the cationic charges is negligible with respect to that of bicarbonate.

## DISCUSSION

Studies such as this one carried out with a very limited investment and during a relatively short period should be interpreted in the light of benchmark papers summarizing long observation periods with detailed measurements regarding all input and output parameters such as Likens and al. (1972).

In this manner, one can concentrate on the aspects that are distinctive of the ecosystem and of the approach chosen within the general framework of the watershed-ecosystem study method.

We may thus accept as well substantiated by other observations, the fact that the ionic concentration remains constant with a narrow range with respect to the changes in stream discharge.

Fluctuations within the range of composition are related to rainfall and stream discharge and consequently to residence time of the solution within the soil system.

Three main processes may be considered as responsible for determining the composition of the soil solution and consequently that of seepage water :

- ion exchange or hydrolysis of exchangeable cations,
- solubilization and precipitation reactions,
- metabolic activity of soil biomass (ion uptake and  $\text{CO}_2$  evolution).

Starting with the last process which has been recently studied by several authors (Miotke (1974), De Jong and Schappert (1972), Rightmire (1978), it seems well established that the concentration of bicarbonate in water leaving the upper soil horizons will be determined by the  $\text{CO}_2$  partial pressure in the gas phase of the soil pores. The latter will be in turn determined by temperature (Gerstenhauer, 1972) and by the rate of exchange of  $\text{CO}_2$  between the soil pores and the atmosphere. The latter being in turn determined by the flushing of soil gases from the soil pores by heavy rainfall falling on an already moist soil, as shown by Miotke (1974). This is apparent in fig. 4 where back calculation of the  $\text{CO}_2$  partial pressure in the soil pores depends as expected on rainfall and above all on a source of easily decomposable organic matter provided by leaf fall during the Autumn. Even during Wintertime at temperature near the freezing point, the partial pressure of  $\text{CO}_2$  is noticeably higher than the atmospheric value of  $3 \times 10^{-4}$  atm. These two factors would offset the effect of temperature which was the most important in the study of Gerstenhauer (1972).

Increased hydrogen ion concentration in the soil water may lead to exchange processes. The exchange affinity of  $\text{H}_3\text{O}^+$  ions is between that of  $\text{Na}^+$  and  $\text{K}^+$  (Gilbert et Laudelout, 1964). The essential difference between this exchange process and that caused by other cations is that it is essentially irreversible (Beckman & Laudelout, 1961).

The soil solution will thus be enriched in bicarbonates of cations in the proportion they had on the exchange complex if their exchange affinity is identical as is the case for  $\text{Ca}^{++}$  and  $\text{Mg}^{++}$ . This is closely verified by the data presented above for these two cations.

$\text{H}^+$  ions remaining on the ion exchanging surfaces will quickly react with the aluminosilicate lattice and cause the appearance of exchangeable  $\text{Al}^{+++}$  which will be less easily displaced than alkali or earth alkali cations and keep on impressing an acid character to the soil.

The fact that the K/Na ratio becomes reversed in stream water with respect to that found in the upper horizon of the forest soils could be purely physiological. The fact that it does not show seasonal influence such as nitrate does points rather to a specificity of the ternary exchange process between hydronium, sodium and potassium on an illitic clay in the presence of a large proportion of earth alkali and aluminium cations. In spite of the considerable agricultural and ecological interest of this exchange, information seems to be lacking.

## REFERENCES

- De Jong E. and Schappert H.J.V. 1972. Calculations of soil respiration and activity from  $\text{CO}_2$  profiles in the soil. - Soil Sci. 113 : 328-333.
- Denaeyer-De Smet S. 1966. Recherches sur l'écosystème forêt. La chênaie mélangée de Virelles-Blaimont. Bilan annuel des apports d'éléments minéraux par les eaux de précipitation sous couvert forestier dans la forêt caducifoliée de Blaimont. - Bull. Soc. Roy. Bot. Belg. 99 : 345-375.
- Denaeyer-De Smet S. 1969. Recherches sur l'écosystème forêt. La chênaie mélangée calcicole de Virelles-Blaimont. Apport d'éléments minéraux par les eaux de précipitation, d'égouttement sous couvert forestier et d'écoulement le long des troncs (1965, 1966, 1967). - Bull. Soc. Roy. Bot. Belg. 102 : 355-372.
- Duvigneaud P. and S. Denaeyer-De Smet. 1964. Le cycle des éléments biogènes dans l'écosystème forêt (Forêts tempérées caducifoliées). - Lejeunia 28 : 1-148.
- Duvigneaud P. and S. Denaeyer-De Smet. 1970. Biological cycling of minerals in temperate deciduous forests. In : D.E. Reichle (Ed.). Analysis of temperate forest ecosystems. - Springer Verlag 199-225.
- Duvigneaud P., S. Denaeyer-De Smet, P. Ambroes et J. Timperman. 1971. Recherches sur l'écosystème forêt. La chênaie mélangée calcicole de Virelles-Blaimont. Biomasse, productivité et cycle des éléments biogènes dans un écosystème "chêne mélangé" (Querceto-carpinetum calcicolum). Essai de phytogéochimie forestière. - Mem. Inst. Roy. Sci. Nat. Belg. no. 164.

Beckman J.P. and H. Laudelout. 1961. Chemical stability of hydrogen-montmorillonite suspensions. - Kolloid-Zeitschrift 2 : 99-107.

Gerstenhauer A. 1972. Der Einfluss des  $\text{CO}_2$  - Gehaltes der Bodenluft auf die Kalklösung. - Erdkunde 26 : 116-120.

Gilbert M. and H. Laudelout. 1964. Exchange properties of hydrogen ions in clays. - Soil Sci. 100(3) : 157-162.

Likens G.E., Bormann F.H., Pierce R.S., Eaton J.S., Johnson N.M. 1977. Biogeochemistry of a forested ecosystem. - Springer Verlag.

Miotke F.D. 1974. Carbon dioxide and the soil atmosphere. - Abh. Karst Höhlenkunde Ser. A. 91 : 1-49.

Nordstrom D.K. 1982. The effect of sulfate on aluminium concentration in natural waters : some stability relations in the system  $\text{Al}_2\text{-O}_3$  -  $\text{SO}_3\text{-H}_2\text{O}$  at 298 K. - Geochim. Cosmochim. Acta 46 : 681-692.

Rightmire C.T. 1978. Seasonal variation in  $\text{PCO}_2$  and  $^{13}\text{C}$  content of soil atmosphere.-Water Resources Res. 14 : 691-692.

Roisin P. 1962. Contribution à l'étude de la végétation forestière des confins occidentaux du Massif Ardennais. - Bull. Inst. Agron. et Sta. Rech. Gembloux 30 : 387-457.

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